Exercise 1 Molecular Mechanics

a) MM only gives information about deviation from an ideal bond, angle, etc. and no information about the bond energy. We can hence not compare isomers which have a different bonding structure.

b) A frequency calculation is based on the Hessian, solving an eigenvalue problem. Possitive frequencies are only obtained for all $3N-6$ coordinates if the system is in a mimimum. The mimimum using a fast model does not need to coincide with the minimum of the more accurate model.

Exercise 2 TIPS: water model

a)

b) $r_{OH} = 0.9572$Å, angle $= 104.52°$ and $q_O = -0.80$ We put the origin in the O atom. Since H_2O is neutral, the answer is independent of the choice of the origin. Dipole is along the bisector. $2 * 0.4 * \cos(104.52/2) = 0.4897$ eÅ

c) There is only an interaction between the O atoms of both dimers.

$$U = A^2/r^{12} - C^2/r^6$$

$$\frac{\mathrm{d}}{\mathrm{d}t}U = -12A^2/r^{13} + 6C^2/r^7 = 0$$

$$12A^2r^7 = 6C^2r^{13}$$

$$6A^2/C^2 = r^6$$

$$r = (6 * 580e3/525)^{1/6} = 4.3341\text{Å}$$

The electrostatic interaction will make it more attractive and hence the r should be smaller

d)

$$\theta_A = -104.52/2°, \theta_B = 27°$$

$$U_{\mathrm{dip-dip}} = -332 \times 0.4897^2/R^3 \left(2\cos\theta_A\cos\theta_B - \sin\theta_A\sin\theta_B\cos\phi\right) = -58.256/R^3$$

e)

$$\frac{\mathrm{d}}{\mathrm{d}t}U = -12A^2/r^{13} + 6C^2/r^7 - 3C_d/r^4 = 0$$

$$-12A^2 + 6C^6r^6 - 3C_dr^9 = ax^2 + bx^3 - c = 0$$

$$x = r^3; a = 6C^6; b = 3C_d; c = 12A^2;$$

$$x = \frac{p}{6b} + \frac{2a^2}{3bp} - \frac{a}{3b}$$

with

$$p = \left(108cb^2 - 8a^3 + 12b\sqrt{3c(27cb^2 - 4a^3)}\right)^{\frac{1}{3}}$$

$$r = 3.0750\text{Å}$$

Exercise 3 Optimizing a H_2O dimer

(a) Total DOF: $3N - 6 = 12$ Internal DOF for one $H_2O = 3$.
DOF for rigid molecules: 12 - 2*3 = 6

(b) $3N = 18$

(c) Force is the first derivative of the potential. H atoms only feel Coulombic interactions. O atoms feel repulsion, dispersion and Coulombic interactions.

(d)

$$U_{\text{disp}} \propto r^{-6} \longrightarrow F \propto r^{-7}$$

$$U_{\text{rep}} \propto r^{-12} \longrightarrow F \propto r^{-13}$$

$$U_{\text{Coul}} \propto r^{-1} \longrightarrow F \propto r^{-2}$$

(e) For rigid molecules, the molecules would fall apart, since the individual atoms can move freely.

(a)

(b) 2*3+1=7 DOF. This is not a problem since one angle would just lead to degenerate results, but the molecules would stay intact.